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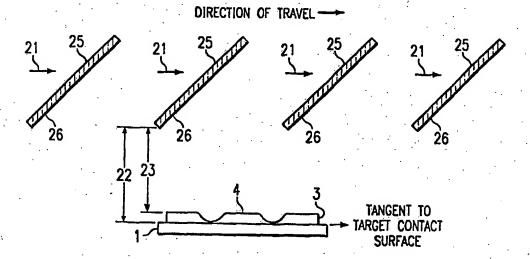
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(54) Title: MAGNESIUM OXIDE SPUTTERING APPARATUS



(57) Abstract

This invention relates to a method and apparatus for high rate reactive sputtering. Particularly, the invention relates to a method and apparatus of sputter depositing reacted metal—compound films where the sputter deposition rate approaches the deposition rate of the unreacted metal. More particularly, the invention relates to an apparatus wherein the sputter deposition target is placed at a greater than usual distance from the substrate and the target metallic erosion track is confined to a narrower width than is typical in current systems.

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MAGNESIUM OXIDE SPUTTERING APPARATUS

TECHNICAL FIELD OF THE INVENTION

Thin film coatings have many uses, including flat panel displays, energy control coatings on glass, optical interference filters, and numerous applications in semiconductors. A vacuum evaporation process is often used to deposit thin films. This process can handle many kinds of material at very high rates but has difficulty applying them with adequate uniformity over large areas. Chemical vapor deposition has also been used but has similar drawbacks to evaporative processes plus a particulate contamination problem for high rates of gas phase reactions. An alternate process known as magnetically enhanced sputter deposition provides good uniformity but is not faster than evaporative coatings for most reacted metal compounds. In particular, many metal oxides sputter quite a bit more slowly than a pure metal when using sputter deposition. This slowness is a well-recognized problem, and numerous solutions have been proposed. See, for example, U.S. Patent No. 4,851,095 issued on July 25, 1989, to Scobey and others. The present invention relates to a method and apparatus for sputter deposition of metal oxides or other compounds at enhanced rates.

In a sputter deposition process, the article to be coated, called the substrate, is placed in a chamber with a gas pressure significantly below one atmosphere. A typical sputter deposition pressure is about 2×10^{-3} torr (0.3 pascal). The gas used is typically argon in non-reactive sputtering, or a blend of argon and a reactive gas for reactive sputtering.

The material to be sputtered onto the substrate is called the target. Typically, the target is electrically connected to be the negative side of a direct current (DC) electric potential. The potential between the anode and the target is typically between 100 and 1000 volts. Alternatively, pulsed DC may be used, where the potential on the cathode makes very short, slightly positive pulses to discharge insulating areas of the

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target surface, which helps prevent arcing, but the target remains predominately negative for the majority of the time. Also alternatively, radio frequency power may be used, but the target again remains predominantly negative. Combinations of radio frequency and DC power supplies have also been used.

The electric field between an anode and the target ionizes the gas in the chamber. The gas ions are driven by the electric field into the target with sufficient energy to dislodge the target material. The rate at which target material is dislodged from the target is called the erosion rate. The dislodged material is electrically neutral and travels from the target to the substrate where it forms the thin film coating.

Until the 1970's, many forms of planar sputter deposition were slow processes, because no effective way to contain electrons close to planar targets had been developed. At that time, magnetically enhanced planar magnetron sputter deposition was invented. The use of properly aligned magnets created a magnetic containment field for electrons. By containing the electrons, the electric power per unit area and the speed of the sputter deposition process were significantly enhanced. Magnetic electron containment fields have also been used to increase the deposition rate of rotating cylindrical targets. For planar targets, the magnetic field defines an erosion width where the target material is preferentially eroded.

Sputter deposition works well when the material being sputtered is a metal and the thin film that is desired is a layer of the same metal. However, in some applications, it is desirable to have a thin film that is the product of a chemical reaction between a metal and a reactive gas such as oxygen or nitrogen. Such films are often produced by sputtering a metal target in a reactive atmosphere, which is typically a combination of argon and the desired reactive gas. Such a process is termed "reactive sputtering." For simplicity, oxygen will be used as the typical reactive gas; however, the discussion applies equally to other reactive gases such as fluorine, nitrogen, other gas compounds, or elements.

The introduction of oxygen into the sputter deposition chamber causes several problems on the target. First, the oxygen will react with the exposed metal of the target.

Then when the argon ions impact the metal oxide at the target surface, they sputter less metallic material because the energy required to break metal-to-oxygen bonds is typically much greater than the energy to break metal-to-metal bonds. The "sputter yield" or the amount of material sputtered per argon ion is typically less for metal oxides than for the metal alone (as shown in Table 1). Further, in the case of reactive sputtering, energy is wasted sputtering the oxygen itself only to have the possibility of oxygen gas reoxidizing these newly exposed metal sites. Further, arcing can occur as an electrically insulating metal oxide layer covers portions of the metal target. The term for these problems, caused by oxygen reacting with the surface of a metallic target, is "target poisoning." The rate at which a target becomes poisoned is a function of the erosion rate, the rate of reaction of the target material with oxygen and the oxygen pressure. At a constant target power, the wider the erosion width, the lower the local erosion rate per unit area is, and the greater the problem of target poisoning is.

TABLE 1

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The sputter yield (sputtered atoms or molecules per argon ion) of oxides is typically, but not always, low compared to the metals. The yield is perhaps influenced by the chemical bond strengths, which are reflected in the temperature required to reach a vapor pressure:

| 20 | | Sputter | Yield | Metal | Sputter Yield | | |
|----|-------|------------|------------|--------------------------------|---------------|------------|--|
| | Metal | (a) 600 eV | (b) 500 eV | <u>Oxide</u> | (a) 600 eV | (b) 500 eV | |
| • | Al | 1.24 | 1.0 | Al ₂ O ₃ | 0.18 | 0.05 | |
| | Cr | 1.30 | 1.2 | Cr ₂ O ₃ | 0.18 | | |
| • | Mg | 0.52 | | MgO | 0.36 | · · · · | |
| 25 | Fe | 1,26 | 0.8 | Fe ₂ O ₃ | 0.71 | | |
| | . Si | 0,53 | 0,5 | SiO ₂ | 1.34 | 0.23 | |

(a) Sputter yield data for 600 eV Ar⁺ ions, Glow Discharge Processes, Brian Chapman, pp. 394-396, Wiley, NY (1980)

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(b) Sputter yield data for 500 eV Ar ion beams, Ion Beam Etch Rates and Sputter Yields, Commonwealth Scientific Corp., Alexandria, VA (~1994)

The problems with reactive sputtering are exacerbated by the high secondary electron emission characteristic of many metal oxides. Energy is wasted accelerating these electrons from the negative cathode target to the anode. The comparison of metals to metal oxides is shown in Table 2 for secondary electrons due to electron impact, but the situation is believed to be analogous for argon ion impact:

TABLE 2

Maximum secondary electron emission (electrons per electron) from electron impact.

| | Max Secondary | Metal | Max. Secondary | | |
|-------|-------------------|------------------|--------------------------|--|--|
| Metal | Electron Emission | <u>Oxide</u> | Electron Emission | | |
| Al | 1.0 | Al_2O_3 | 2 to 9 | | |
| Ве | 0,5 | BeO | 3.4 | | |
| Mg | 0.95 | MgO | 20 to 25 | | |
| Si | 1.1 | SiO ₂ | 2.1 to 4 | | |

Secondary Electron Emission, pp. 12-115 to 12-116, CRC Handbook of Chemistry & Physics, 75th Edition, D. R. Lide, CRC Press (1994).

An extreme example of a metal oxide that has a low sputter yield and a high secondary electron emission is magnesium oxide. Magnesium oxide is chosen for use as the final layer in plasma displays because of these two properties. The high secondary emission lowers the operating voltage of the display and the low sputter rate increases the lifetime of the display. The plasma display system is, in fact, quite similar to a miniature sputter deposition chamber. In a plasma display, an electrical potential between electrodes causes an inert gas to ionize and emit light, either directly for monochrome displays or by interacting with a phosphor for color displays. Thus, for long plasma display lifetimes, it is particularly desirable to have a final layer of a metal

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compound that is inherently slow to sputter. Consequently, many final layers in plasma display systems are manufactured by using an evaporative process rather than sputter deposition. It is foreseen that plasma displays have the possibility of having the niche of very large displays. Displays with a diagonal size of 106 cm are being manufactured now, and displays with a diagonal size of 152 cm are contemplated. It is envisioned that the evaporation process will be impractical for high production volumes of these large sizes because of the difficulty of maintaining uniform layer thicknesses as panel size increases.

Thus, there is a need for an apparatus and method of manufacture which have the benefit of relatively high speed and uniformity over large areas typically associated with sputter deposition of metals, but which can be used with reactive metal compounds.

Various solutions to the slow deposition rate of reactive metal compounds have been proposed. For example, The Optical Coating Laboratory, Inc. in Santa Rosa, California, has developed a process called "meta mode" coating. The meta mode coating process sputter deposits about one atomic layer of a metal in one chamber and then, in the next chamber, exposes the thin metal layer to the reactive gas to create the reacted metal compound. This process cycles back and forth between chambers until the desired thickness of reacted metal compound is obtained. Other solutions to the slowness of reactive sputtering include pulsed introduction of the reactive gas species and attempts to segregate the sputtering gas from the reactive gas within the sputtering chamber. While these approaches can increase the deposition rate of reacted metal compounds, they do not produce by simple methods an overall deposition rate that approaches the deposition rate of the metal itself.

General Geometry

Typically, a planar sputter deposition target is eroded in a "racetrack" pattern. The width of the racetrack is made large to increase the amount of target material available to be sputtered before the target has to be replaced. Each portion of a typical racetrack is approximately 4 cm wide. Thus, a total of approximately 8 cm of target

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width is subject to erosion, because a substrate typically moves past the target in a direction that crosses two portions of the racetrack. The portion of the target that is not subject to erosion is quickly covered with the reacted metal compound.

To conserve volume, and thus vacuum system requirements, the separation distance between the target and the substrate is generally kept low. For example, in the manufacture of conducting electrodes for plasma display screens, a target-to-substrate separation of 7 cm is common. The target-to-substrate separation for large scale architectural glass coating equipment is typically no more than 20 cm.

Background and Concepts

A substrate moving near a long magnetron sputter source receives a uniform thin film on the surface facing the target. The substrates typically pass through an air-to-vacuum lock, travel past the target, and pass through a vacuum-to-air lock. "In-line sputtering" is the term for this configuration. The "throw" distance is the shortest approach or distance of the substrate to the erosion region of the target. For long line sources, the maximum local deposition rate per unit area on the substrate is roughly proportional to the inverse of the throw distance.

The reaction of gases with the target metal is thought to occur at the surfaces of the target and the growing film instead of occurring in transit for two reasons: First, the metal atoms usually spend more time exposed to the reactive gas on the target and substrate surfaces than in transit between the target and the substrate. Second, the joining of a metal atom with a reactive atom in transit, while satisfying conservation of both energy and momentum, is unlikely.

Another attribute of sputter deposition is the difficulty of maintaining a pressure differential between the target and the substrate. Reasonably-sized vacuum pumps allow only a small flow of gas. For instance, the pumping speed, S, of a 25 cm diameter pump at the sputter chamber is on the order of 1000 liters per second. At a typical sputter pressure, P, of 0.3 pascal, the total gas flow is S x P or only 300 pascal liters per second. On the other hand, the vacuum conductance between the target and the substrate is usually quite large. For a 145 cm x 15 cm target surface and a substrate surface area of

145 cm x 100 cm, the vacuum conductance is on the order of 100,000 liters per second from the target to the substrate (averaging the two areas and using an aperture conductance per unit area of 11.6 liter/second/square cm). If all of the 300 pascal liters per second of gas were introduced in the region of the substrate, the pressure difference between the substrate and the target could only be 1/100 of the sputter pressure or 0.003 pascal. Interjecting hardware between the target and the substrate to cut down on the conductance between the two has the disadvantage of intercepting sputtered material before it reaches the substrate. Because the reactive gas pressure is approximately the same at the target as at the substrate, it is inherently difficult to keep the surface of the target significantly unoxidized while substantially oxidizing the growing film. So, the approach to solving the reactive sputtering problem by maintaining a high reactive gas pressure near the substrate and a low reactive gas pressure near the target is fraught with difficulty.

SUMMARY OF THE INVENTION

Narrow Erosion Path

One aspect of the present invention is the reduction in width of the erosion path on the target. When metal in the erosion path reacts with the reactive gas, the previously described problems (including arcing, wasted energy sputtering the reactive compound instead of the metal, and wasted energy of secondary electrons) occur. By narrowing the erosion track, a higher power density per unit area can be applied, resulting in higher erosion rate per unit area. The increased power density per unit area may increase the target reaction rate slightly by increasing the temperature of the target surface and by activating the oxygen by the increased discharge current density per unit area next to the target surface. However, the predominant effect is to erode the target more rapidly and leave the target surface more metallic. By reducing the width of the erosion path, the ratio of reacted metal to unreacted metal in the erosion path can be reduced, and the poisoning of the target lessened.

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A simple method of controlling the width of the erosion track utilizes magnetic pole pieces to define the edges of the erosion path. These magnetic pole pieces may be made of a ferromagnetic material such as iron or may be made of other materials that have a magnetic permeability greater than the target material. Preferably, the beveled edges of iron plates are placed in proximity to the desired erosion track boundaries. Even if the iron is placed on the surface of the target, the iron is so effective in defining the erosion edge that the iron itself is not eroded substantially. If erosion of the iron is a significant concern, the iron can be inset below the surface of the target, coated with the target material, or may be electrically isolated from the target by being placed slightly off the target so as not to be at the same electrical potential as the target. Other materials that will shape the magnetic field and define the erosion path include nickel, cobalt and alloys of iron, nickel and cobalt.

Increased Target-to-Substrate Distance

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Simply decreasing the width of the erosion track improves the operation at the target but does not by itself increase the deposition of the reactive metal compound. In fact, the higher output of pure metal atoms can lead to the deposition of an undesirable metallic layer rather than the desired reacted metal compound. Moving the target significantly further away than usual from the substrate reduces the deposition rate per unit area on the substrate. This decrease in deposition rate effectively provides additional time for the reaction to occur on the substrate where the reaction is desirable. At the same time, the total area over which deposition is occurring is typically increased. By increasing the distance between the target and the substrate and reducing the deposition rate per unit area, but increasing the area where deposition occurs, the film thickness on a substrate moving adjacent to the target remains substantially the same, but more reaction occurs at the film.

Geometric Tradeoffs

Decreasing the erosion path width decreases the available inventory of target material. Increasing target-to-substrate distance exacerbates thickness fall- off on substrates moving near the end of a long target such that a longer target than usual may be required. So, a combination of the two geometry changes is probably desirable rather than an extreme change in only one.

It is convenient to think in terms of the ratio of the deposition area to the erosion area. This invention increases this area ratio above typical ratios. The reactive gas pressure is adjusted to obtain the desired degree of reaction on the substrate without poisoning the target. If this adjustment cannot be achieved, the area ratio probably needs to be increased.

For targets that are long compared to the throw distance, a nearly equivalent ratio is the ratio of the target-substrate distance to the total of the erosion path widths. Likewise, if the reactive gas cannot be adjusted to give the desired degree of reaction on the substrate without poisoning the target, then this distance ratio probably needs to be increased.

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The above area and distance ratios allow economic modeling of the geometric tradeoff. Making the erosion path narrower decreases the inventory of target material, and increases downtime for target changes and perhaps increases direct material costs. Increasing the throw distance typically requires longer targets to obtain film uniformity near the target ends, and results in higher capital costs and direct material costs.

It is believed that the minimum acceptable ratios discussed above are primarily dependent only on the desired degree of reaction of the material and not so much on the material itself. In the case of a different material or different reactive gas, the reactivity of the surface of the target may be more or less than the case for magnesium and oxygen. However, the reactivity at the film surface will also be more or less by approximately the same degree. For example, magnesium oxide should probably be completely oxidized for use in plasma panels, and a distance ratio of 16 has been found to just accomplish this complete oxidation. It is believed that a completely oxidized film of aluminum oxide could be produced with similar geometry. However, indium tin oxide ("ITO"), a transparent conductor common in many flat panel displays, has its best properties when the ITO is oxygen deficient. It is believed that ITO could be produced efficiently with a distance ratio less than 16.

Another factor which may decrease the distance ratio is elevating the substrate temperature substantially above the target surface temperature. The reactivity of the hotter film surface may be higher than the reactivity of the target such that the desired film reaction may be obtained with a lower distance ratio.

A phenomenon that occurs with indium-tin, indium tin oxide, zinc, and other target materials is the formation of "black nodules" on the surface of the target after substantial target erosion. These nodules are apparently sputter resistant, raised areas. The nodules are typically flat black in appearance, perhaps from an increased oxidation of the nodule, but more so from the rough texture of deposited material on the sides of the nodules. The density of black nodules can become so great that the overall erosion rate of the target can be reduced.

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It is known that an increase of surface temperature of an ITO target surface to about 300°C dramatically reduces black nodules. So, an increase in power density per unit area with the use of pole pieces can allow the increase in surface temperature for ITO targets such that black nodules are greatly reduced.

The Geometrically Enhanced Metal-Compound Sputtering (GEMS) Configuration

The GEMS configuration of this invention increases the throw distance beyond normal so that the film deposition rate in any region on the substrate is lower. Likewise, the erosion path on the sputter target is narrower. One method of confining this erosion width is to add iron pole pieces to the surface of the target. At a given electrical sputter power, the power density per unit area and the erosion rate per unit area become large where iron pole pieces are used. The overall configuration of this invention increases the ratio of the erosion rate per unit area to the deposition rate per unit area by increasing the area over which the deposition occurs and decreasing the area over which erosion occurs.

Result of the Invention

By the use of beveled iron pole pieces, reducing the width of the erosion path, and increasing the separation of the target and substrate, the surface of the target in the erosion path remains relatively unreacted, while the film is substantially reacted. The higher erosion rate of the relatively unreacted surface allows the energy efficiency (volume of material sputtered per unit of energy) of this improved sputtering process to be on the order of five higher than conventional reactive sputtering for magnesium oxide films. The energy efficiency improvement is highly material specific and depends on the ratio of energy efficiency of sputtering the metal to the efficiency of sputtering the reacted metal.

Forcing the target surface to stay more metallic reduces the amount of insulating regions on the target surface and reduces the rate at which these regions form. The frequency of arcing to these insulating regions is typically reduced by one to two orders of magnitude.

Another phenomenon of reactive sputtering is the coating of the anode with insulating material. Despite attempts to "hide" the anode with labyrinths, the anode usually eventually gets coated. This phenomenon is called the "disappearing anode effect" and can cause arcing and can even cause the extinguishing of the electrical discharge. With the present invention, by positioning the anode in close proximity to the target, the film on the anode can be made to be substantially electrically conducting. The glow discharge is then much more stable.

With this invention, the vapor efficiency or amount of material sputtered per unit of energy can be improved for magnesium oxide by a factor of about 5 and the thickness of a film can be improve by a factor of about 3.5. For example, with this invention, a substrate moving by one long cathode at a speed of 0.1 meter per minute and at a lineal cathode power density of 2.95 kW per meter, acquires a magnesium oxide film thickness of 175 nm. A conventional method under the same speed and power density receives a thickness of only 49 nm.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a typical planar magnetron sputter deposition arrangement.

Figure 2 shows a planar sputter deposition arrangement within the invention in which the substrates travel past a target at an angle.

Figure 3 shows a third alternative planar magnetron sputter deposition arrangement in which the planar target is arranged at an angle to the substrates.

Figure 4 shows a cylindrical magnetron sputter deposition apparatus.

Figure 5 shows an alternative arrangement for a cylindrical magnetron sputter deposition apparatus.

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DETAILED DESCRIPTION OF THE INVENTION

Figure 1 discloses a planar magnetron sputter deposition arrangement according to the invention. In such an arrangement, the target 3 is placed in contact with the target holder 1 at the target contacting surface 2. The target may be bonded to the target holder or may be attached using mechanical means such as screws (not shown). The target surface 4 is subject to erosion by being bombarded with ions 10. The target 3 is eroded through an erosion path 6 having erosion path widths 5a and 5b defined by the magnetic fields created by magnets 7, which are attached to plate 13.

Erosion path widths are preferably similar, and preferably not greater than about 4 cm each, for a total erosion path width of not more than about 8 cm. More preferably, each of erosion path widths 5a and 5b are not greater than about 3 cm for a total erosion path width of not more than about 6 cm. Even more preferably, each of erosion path widths 5a and 5b are not more than about 2 cm for a total erosion path width of not more than about 4 cm. Most preferably, each of erosion path widths 5a and 5b are not greater than about 1.5 cm for a total erosion path width of not more than 3 cm.

A substrate carrier 20 holds substrate 25 and moves the substrate 25 in a direction 21 relative to erosion paths 5a and 5b. Generally, but not necessarily, direction 21 is perpendicular to the centerline of erosion paths 5a and 5b. The substrate carrier 20 has a substrate contacting surface 24 spaced a distance 22 from the target contacting surface 2. Distance 22 is the minimum distance from target contacting surface 2 to substrate contacting surface 24.

Preferably, distance 22 is not less than about 31 cm. More preferably, distance 22 is not less than about 41 cm. Most preferably, distance 22 is not less than about 46 cm.

In operation, substrate 25 has a surface 26 spaced a distance 23 from the target surface. Distance 23 is the minimum distance from the target surface to the substrate surface that is being coated and is called the "throw distance." Preferably, distance 23 is not less than about 30 cm. More preferably, distance 23 is not less than about 40 cm.

Even more preferably, distance 23 is not less than about 45 cm. Most preferably, distance 23 is not less than about 47.5 cm.

Target material 11 travels from the target 3 to the substrate 25. Reactive gas 12 reacts with target material 11 at the substrate surface 26 and at the target surface 4. Optionally, material with a magnetic permeability greater than the magnetic permeability of the target 3 is placed in proximity to the target surface 4. These optional pole pieces 9 shape the magnetic field to define the erosion path width.

Figure 2 shows an arrangement similar to Figure 1 but wherein the substrates being coated are oriented at an angle to the planar target. The substrate carrier, optional pole pieces and magnets are not shown in Figures 2 and 3. While the orientation in Figure 1 is more typical, the orientation in Figure 2 is within the invention. Likewise, Figure 3 shows a planar magnetron sputter deposition apparatus in which the target is oriented at an angle to the substrate direction of motion. The orientation in Figure 3 is also within the invention.

Figures 4 and 5 disclose planar magnetron sputter deposition arrangements in which the target material is placed on a rotating cylinder. In some configurations, the cylindrical target material is self-supporting and does not have an additional support cylinder. Likewise, the configurations of Figures 4 and 5 is within the invention.

Optional pole pieces are not shown in Figures 4 and 5. Both Figures 4 and 5 show the condition where the target is not rotated so that the erosion path width can be measured. In use, the target surface would be eroded uniformly and the erosion paths would not appear as shown in Figures 4 and 5.

To determine the erosion path width for a cylindrical magnetron, the target material must be in a fixed, non-rotating position. While this is not typical for manufacturing processes, it is necessary for the measurement of the criteria called for in this invention. Once the measurements are obtained, the cylindrical target would be rotated during use as with prior processes. The erosion path width for a planar magnetron is determined for purposes herein by measuring the point at which the

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erosion is 2% of the total erosion at the erosion path center based on a planar projection. When magnetic pole pieces are not used, the erosion path width for a cylindrical magnetron is measured by comparing the maximum deviation from the original cylindrical dimension and measuring the length of an arc from the point at which 2% of the material has eroded compared to the maximum erosion height.

When magnetic pole pieces are placed in proximity to the surface of the cylindrical target to control the width of the erosion track, the erosion track width is defined as the average distance between the edges of the magnetic pole pieces. When using cylindrical targets, it is preferred that the magnetic pole pieces not be in contact with the surface of the target and that they be adequately cooled to maintain their dimensioned stability.

When using a cylindrical target as in Figure 4, the throw distance 23 is measured from the surface of the target to the surface of the substrate. When a self-supporting target is used, the inside surface is used as the target support surface.

When using a cylindrical target where the erosion paths are placed at an angle as is illustrated generally in Figure 5, the throw distance is measured from the surface of the target in the middle of the erosion path nearest the substrate to the surface of the substrate. For self-supporting targets, the distance from the target support surface to the substrate support surface is measured from a point on the inside surface of the target where a line from the axis of the target through the midpoint of the erosion path closest to the substrate intersects the inside surface of the target.

Although the invention can be used with cylindrical targets rotating at typical rates, an additional benefit is obtained by reducing the rotation rate of the target.

Typically, cylindrical targets rotate at rates of 10 revolutions per minute (RPM) or more. Generally, the slower the rotation rate, the more completely the target surface will oxidize where it is not in the erosion path. Surprisingly, when using the narrow erosion

path width of the invention, a slower rotation rate causes the erosion path to be substantially metallic as described above for planar sources.

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For the purposes of this invention, the erosion duration in seconds is defined as the erosion path width divided by the product of the rotation speed times the inner circumference of the cylinder of target material. Thus, a cylindrical target with an inner diameter of about 13 cm, a rotation rate of 10 RPM and an erosion path width of 4 cm will have an erosion duration of about 0.6 second $((4.60)/(5.\pi\cdot10))$.

Preferably, the erosion duration is not less than one second. More preferably, the erosion duration is not less than 5 seconds. Even more preferably, the erosion duration is not less than 10 seconds. Most preferably, the erosion duration is not less than about 15 seconds.

GEOMETRICALLY ENHANCED METAL-COMPOUND SPUTTERING Preferred Distance Ratio

The "optimum" ratio of throw distance to total erosion width varies with application and the degree of oxidation desired in the film. Preferably, the ratio of throw distance 23 to total erosion path width 5a and 5b is not less than about 4. More preferably, the ratio of throw distance 23 to total erosion path width is not less than about 7. Even more preferably, the same ratio is not less than about 10. Most preferably, the ratio of throw distance 23 to total erosion path width 5a and 5b is not less than about 15.

The "deposition area" is herein defined as the area where the deposition rate per unit area is at least 1/2 of the maximum rate per unit area. Preferably, the ratio of deposition area to erosion area is not less than about 5. More preferably, the ratio of deposition area to erosion area is not less than about 9. Even more preferably, the ratio of deposition area is not less than about 14. Most preferably, the ratio of deposition area to erosion area for complete oxidation of the film appears to be about 18.

The above "optimum" ratios are considered to give "reasonable" results while using a feedback control, as described below, and while producing magnesium oxide films. It is believed that other film materials with complete oxidation could be produced

with similar ratios. To avoid the use of feedback control, higher ratios would probably have to be used.

Specific Example

The following example relates to magnesium oxide films produced for flat panel plasma displays. Magnesium oxide has a notoriously low sputter rate, which is one of its desirable qualities for use in plasma displays.

Prior to this invention, a typical throw distance would be approximately 8 cm and the sum of the two erosion paths would also be about 8 cm for a distance ratio of about 1. Practicing this invention for magnesium oxide, the preferred throw distance is about 48 cm and the total of the two erosion widths is about 3 cm for a distance ratio of about 16. With this large distance ratio using the invention, the vapor efficiency of the magnesium oxide is almost as large as the magnesium metal vapor efficiency as shown in Table 3. To make this comparison, the thickness of the Mg metal film has been converted to an equivalent magnesium oxide film. Magnesium and magnesium oxide both have the same density, so there is less magnesium per unit volume in a magnesium oxide film than in a magnesium film. The vapor efficiency is the volume of material sputtered and collected on a substrate per unit of sputter energy. The volume is expressed in angstrom centimeters squared. The examples in Table 3 were made using a throw distance of 18.75 inches and an erosion width of about 1.47 cm.

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TABLE 3
Comparison of Mg & MgO

| | | • | • . | Vapor Eff. | | | |
|-----|---------|-----------|-------------|-------------|------------|-----------------|--|
| 5 | Cathode | Thickness | | Wt. | Equivalent | (angstrom· cm²/ | |
| | Film | (volts) | (angstroms) | (grams/mol) | MgO (ang.) | joule) | |
| ·.· | Mg | -460 1350 | 1350 | 24.3 | 2239 | 12.1 | |
| | MgO | -360 | 1700 | 40.3 | 1700 | 11.8 | |
| | MgO | -220 | 250 | 40.3 | 250 | 2.8 | |

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Cathode current = 10 amp. Cathode length = 146 cm.

Substrate speed = 10.2 cm per minute. Density of both Mg and MgO = 1.74 grams per cubic cm.

For contrast, the last row of Table 3 shows a film from a much more oxidized target surface. This sample was made with a large throw distance and a narrow erosion width, but the target was intentionally allowed to oxidize contrary to normal operating conditions. The energy efficiency is much lower, and the magnitude of the voltage was reduced to 220 V by increasing the oxygen flow. For comparison, a competitor obtained a vapor efficiency of 2.38 (angstrom cm²/joule) for magnesium oxide. In comparison to the competitor's process, merely in terms of vapor efficiency, the invention is 5 times as efficient when typical cathode voltages are used. It would appear that the competitor is using an oxidized target surface based on the lower energy efficiency of the competitor's process even compared to the last row of Table 3.

Multiple Cathodes

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Following the design criteria of keeping the deposition rate per unit area low, the spacing between adjacent cathodes should be such that the maximum deposition rate per unit area should not be substantially greater than the maximum for one cathode. For example, if cathodes were closely spaced, the deposition rate per unit area in the coating region between the two cathodes could be nearly twice the maximum rate for only one cathode, and this closely spaced situation could be undesirable.

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Cathode Construction

A 0.70 cm x 14.3 cm x 146 cm magnesium plate is held with machine screws in about 30 locations around the periphery and down the center to a water cooled copper backing plate. Without any other steps to increase heat transfer between the magnesium and the copper, this configuration allows about 4000 watts of sputter power without damage to the target or the target support system.

The magnets are Ceramic 8. The outer magnets are 1.4 cm wide and 2.5 cm in the direction of magnetization. The center magnets are 2.5 cm wide and 2.1 cm in the direction of magnetization. However, the material selection and size are not regarded as critical. The pole pieces concentrate the magnetic field such that there is no foreseen problem in using weak magnets.

The erosion path is narrowed to about 1.5 cm by attaching high magnetic permeability material pole pieces to the sputtered face of the magnesium. Cold rolled 0.32 cm-thick steel pole pieces with a 30° bevel are preferred. The sharp edge of the bevel is dulled to a 0.03 cm radius. Acceptable pole pieces can vary widely in thickness, bevel, and magnetic permeability. However, stronger or wider magnets might saturate sharp pole pieces causing the magnetic field shape to change near the sharp edge. With unsaturated pole pieces, the magnetic field in the middle of the pole piece emerges perpendicular to the pole piece surface; however, this is not the case with saturated poles. It is believed that the unsaturated condition helps the pole pieces more exactly define the edge of the erosion path and prevents erosion of the poles. The pole piece tips in the preferred configuration above are calculated to have a magnetic field strength of about 0.2 tesla, and the saturation of cold rolled steel is about 2.1 tesla.

When pole pieces 9 are used on the surface of the target on both sides of an erosion path, the erosion width is defined as the minimum distance between the edges of pole pieces on opposite sides of an erosion path. When only one pole piece or no pole pieces are used, the erosion width is measured on the target when it has been eroded to the point of needing replacement. A profilometer is used on the spent target to measure the distance from the uneroded surface plane to the eroded surface. The erosion width

is the distance from the place where the profilometer first shows a deviation of 2% of the maximum deviation to the place where it first shows less than 2% of the maximum derivation when measurements are taken in a direction perpendicular to the centerline of the erosion track.

5 Control

With even greater distance ratios than 16, it might be possible to have the target surface even more metallic and avoid feedback control schemes. In such case, the only control might be manual adjustment of sputter power, reactive gas flow, or both. However, with a distance ratio of about 16, reactive gas control is advisable. There are two feedback control schemes found to work quite well. The first scheme senses the cathode voltage, as can be seen in Table 3, reflects the degree of oxidation of the surface of a magnesium target. The second feedback scheme senses the light emission from the glow discharge. Alternatively, a brute force scheme uses very high pumping speed and high reactive gas flows. Each of these control methods is discussed below.

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1. Voltage Control. Planar magnetrons tend to be fairly constant voltage devices over wide ranges of current. However, as noted in Table 3, the voltage is a good indicator of the state of the target surface. There is a monotonic continuum of cathode voltage between the metallic and the oxidized magnesium surface. The voltage that produces substantially oxidized magnesium oxide films with the preferred conditions, as judged by the optical absorption of the films, yet allows a high deposition rate is about -280 to -400 volts. The preferred magnitude of the voltage decreases from the higher value with a new target to the low value as the target is eroded.

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An electrical signal proportional to the cathode voltage goes to a PID loop controller. The operator enters a voltage set point into the PID controller, and the controller adjusts a ratio gas control unit to maintain the desired voltage. The ratio gas controller adjusts one or more gas flow valves to maintain the ratio of flows from one valve to the next at preset values. The ratio gas controller adjusts one to five (two being preferred) oxygen valves of about 20 to 200 (100 being preferred) standard cubic cm

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per minute capacity each. The control loop acts to control the oxygen in order that the cathode voltage remains at the level the operator has set.

A variation of this control scheme uses a fixed oxygen flow set by the operator. The target voltage signal is fed to the PID controller. The operator also enters a voltage set point into the PID controller. The output of the PID unit controls the current of the sputter power supply so as to keep the target voltage at the desired level. An upper current limit is advisable with this scheme.

2. Emission Control. The light from the glow discharge has distinct sharp spectral emission lines from the elements. For example, magnesium has intense 384 and 518 nm lines. Argon and oxygen have very little interference near these wavelengths. The intensity of emission of a line is indicative of the amount of the element present in the discharge. The amount of an element from the target in the discharge depends upon the sputtering rate, which in turn typically depends upon the degree of oxidation of the target. Thus, the intensity of an emission line can be an indirect indicator of the degree of oxidation of the target surface.

A baffle structure passes only light directly from the glow and not light that may be reflecting off moving surfaces, such as substrates, or other surfaces that may change reflectance as coating builds up. This direct light passes through a vacuum to air window and then through a spectral filter (i.e., 518 nm for magnesium), which can be a colored glass or a thin film interference filter, the latter being preferred. The monochromatic light excites a silicon p.i.n. (p-type Si, intrinsic Si, n-type Si) photo detector with an area of about 1 cm². The low current signal is amplified by a current to voltage transamplifier (a low input-impedance picoampmeter typically on a nanoamp scale) and then into a PID controller. The operator enters a set point, indicative of the amount of light desired, into the PID controller. The output from the PID controller goes to a ratio gas flow controller which in turn controls one to ten (two preferred) oxygen valves of preferably 100 standard cubic cm capacity each. The oxygen flow is controlled to maintain the spectral line light at the set intensity.

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For the voltage and light emission control schemes, two vacuum pumps are symmetrically located on each side of the deposition area and each have about 1000 to 5000 (2000 preferred) liter per second pumping speed at the sputter chamber. For a 146 cm long target with a mechanically mounted magnesium plate, the sputter current is typically 4 to 20 amps (12 amps preferred). The oxygen control valves are located close (within 30 cm) of the sputter chamber and the chamber inlets are close (within 50 cm) to the cathode. The gas inlets are uniformly spaced along one side of the cathode. The resultant gas flows under the preferred conditions are about 45 standard cubic cm total oxygen flow and 180 standard cubic cm of argon. Of course, these values can vary widely based upon gas inlet locations with respect to vacuum pumps, chamber geometry, and of course cathode length, power, and target material.

3. High Gas Flow Control. A third, less desirable, control method is to use very high pumping speed vacuum pumps and higher flow of reactive gas. This approach overwhelms the effects of outgassing and the hysteresis well known for the reactive process. This control scheme requires about three times as much gas flow as described above. The high capital and operating costs of very high speed pumps typically make the feedback control schemes described above more cost effective.

WE CLAIM:

- 1. A sputter deposition apparatus comprising a target holder having a target contacting surface, a substrate carrier having a substrate contacting surface and a plurality of magnets placed in proximity to said target holder, said plurality of magnets defining at least one magnetic field defining one or more erosion paths wherein the ratio of the distance from said target contacting surface to said substrate contacting surface divided by the total width of said one or more erosion paths is greater than 4.
 - 2. The apparatus according to claim 1 wherein said ratio is greater than 7.
 - 3. The apparatus according to claim 1 wherein said ratio is greater than 10.
 - 4. The apparatus according to claim 1 wherein said ratio is greater than 15.
 - 5. The apparatus according to claim 1 further comprising a target of material attached to said target holder and having a target surface.
 - 6. The apparatus according to claim 5 further comprising at least one magnetically permeable piece of material having a magnetic permeability greater than the magnetic permeability of said target placed in proximity to the surface of the target to be sputtered.
 - 7. The apparatus according to claim 6 in which said at least one magnetically permeable piece is aligned with at least one magnet placed in proximity to said target holder.
 - 8. The apparatus according to claim 6 wherein said magnetically permeable piece comprises iron, nickel, cobalt, or alloys thereof.

- 9. The apparatus according to claim 6 wherein said magnetically permeable piece comprises a permanent magnet alloy.
- 10. The apparatus according to claim 6 wherein said magnetic permeable material allows greater power density per unit area to be applied to the eroded surface of the target than the power density without said magnetic material.
- 11. The apparatus according to claim 10 wherein said greater power density reduces the amount of black nodules on the surface of the target.

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- 12. A sputter deposition apparatus comprising a target holder having a target-contacting surface and a substrate carrier having a substrate-contacting surface and capable of moving a substrate in a direction relative to the target-contacting surface wherein the closest approach of said target-contacting surface to said substrate-contacting surface is not less than 31 centimeters.
- 13. The apparatus according to claim 12 further comprising at least one magnet placed in proximity to said target holder, said at least one magnet creating a magnetic field that defines a target erosion path having a width not greater than about 4 centimeters wide.
- 14. The apparatus according to claim 12 further comprising a plurality of magnets placed in proximity to said target holder and said plurality of magnets have a plurality of magnetic fields defining a plurality of target erosion paths that have a total width not more than about 8 centimeters in the direction of movement of said substrate carrier relative to said target holder.
- 15. The apparatus according to claim 12 wherein said distance from said target contacting surface to said substrate contacting surface is not less than about 41 centimeters.

- 16. The apparatus according to claim 12 wherein said distance from said target contacting surface to said substrate contacting surface is not less than about 46 centimeters.
- 17. The apparatus according to claim 14 wherein said plurality of target erosion paths have a total width of not more than about 6 centimeters.
- 18. The apparatus according to claim 14 wherein said plurality of target erosion paths have a total width of not more than about 4 centimeters.
- 19. The apparatus according to claim 14 wherein said plurality of target erosion paths have a total width of not more than about 3 centimeters.

20. A process for reactive sputter deposition comprising the steps of: placing at least two magnets in proximity to a target holder establishing a closed magnetic field between said at least two magnets defining one or more erosion paths;

attaching a target having a surface comprised of material to be sputtered to a target holder in a sputter deposition chamber;

establishing an electrical potential between the target and an anode; establishing a reactive sputtering atmosphere;

and

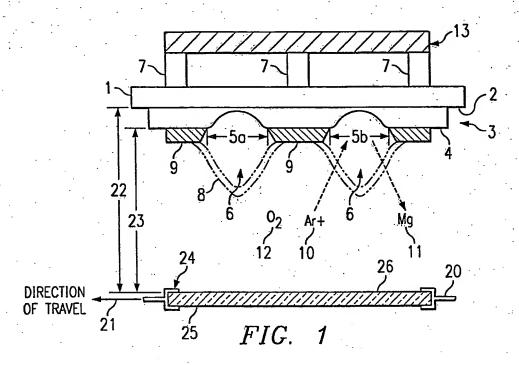
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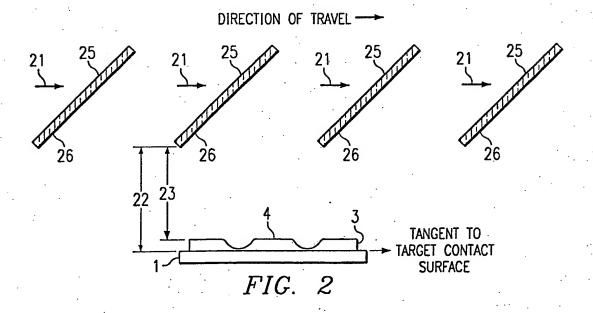
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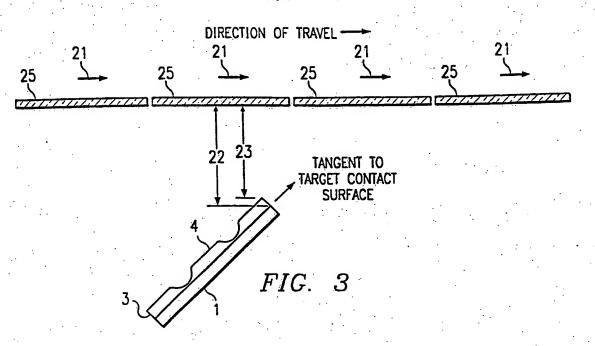
introducing a substrate having a surface to be reactively coated into said sputter deposition chamber wherein the ratio of the distance from said target surface to said substrate surface divided by the total width of said one or more erosion paths is greater than 4.

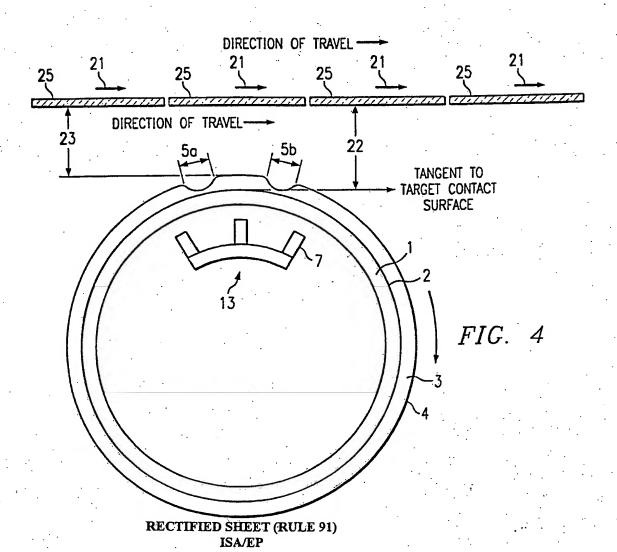
- 21. The process according to claim 20 wherein said ratio is greater than 7.
- 22. The process according to claim 20 wherein said ratio is greater than 10.
- 23. The process according to claim 20 further comprising placing at least one magnetically permeable piece of material having a magnetic permeability greater than the magnetic permeability of said target in proximity to said target surface.
- 24. The process according to claim 23 further comprising aligning said at least one magnetically permeable piece of material with one of said at least two magnets to define an edge of an erosion path

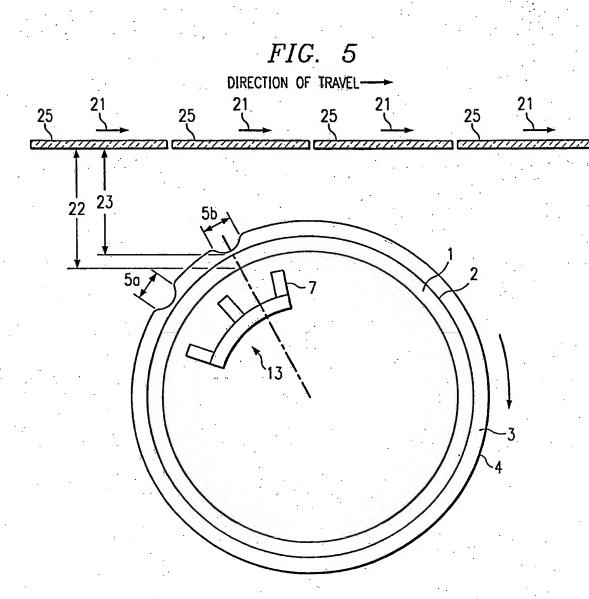
- 25. A sputter deposition apparatus comprising a target holder having a target and a substrate deposition area further comprising a plurality of magnets placed in proximity to said target holder and said plurality of magnets define at least one magnetic field defining an erosion area on said target wherein the ratio of the total erosion area to the substrate coating area is greater than 4.
- 26. The sputter deposition apparatus according to claim 25 wherein a ratio of the substrate coating area to the target erosion area is greater than 7.
- 27. The sputter deposition apparatus according to claim 25 wherein said ratio is greater than 10.
- 28. The sputter deposition apparatus according to claim 25 wherein said ratio is greater than 15.
- 29. The sputter deposition apparatus according to claim 25 further comprising an anode placed in proximity to said target such that the sputtered material collected by said anode remains substantially metallic and substantially electrically conducting.











INTERNATIONAL SEARCH REPORT

ti .atlonal Application No PCT/US 98/05143

| A. CLASSIFIC | CATION OF SUBJECT MATTER C23C14/35 H01J37/34 | | | | | |
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| Electronic dat | a base consulted during the International search (name of data | base and, where practical, search terms used | | | | |
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| C. DOCUME | NTS CONSIDERED TO BE RELEVANT | | | | | |
| Category * | Citation of document, with indication, where appropriate, of the | relevant passages | Relevant to claim No. | | | |
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| Furth | ner documents are listed in the continuation of box C. | Patent family members are listed | in annex. | | | |
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| | actual completion of the international search July 1998 | Date of mailing of the International se 16/07/1998 | arch report | | | |
| <u>·</u> | ailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Fax: (+31-70) 340-3016 | Authorized officer Patterson, A | | | | |

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Information on patent family members

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